The poisoning effect of Na$^+$ and Ca^{2+} ions doped on the V$_2$O$_5$/TiO$_2$ catalysts for selective catalytic reduction of NO by NH$_3$

Fushun Tang, Bolian Xu, Haihua Shi, Jinheng Qiu, Yining Fan [*]

Key Laboratory of Mesoscopic Chemistry of MOE, Jiangsu Provincial Key Laboratory of Nanotechnology, School of Chemistry and Chemical Engineering, Nanjing University, 22 Hankou Road, Nanjing 210093, Jiangsu, China

A B S T R A C T

Deactivation of the supported V$_2$O$_5$/TiO$_2$ catalsts due to deposition of alkali and alkaline earth metal salts in fly ashes is one of the most important problems in the selective catalytic reduction (SCR) of NO$_x$ by NH$_3$. In this work, the poisoning effect of Na$^+$ and Ca^{2+} ions doped on the V$_2$O$_5$/TiO$_2$ catalysts for selective catalytic reduction of NO by NH$_3$ has been studied. It has been shown that the Na$^+$ and Ca^{2+} ions doped can poison the V$_2$O$_5$/TiO$_2$ catalyst and the Na$^+$ ions exhibit greater poisoning effect than Ca^{2+} ions. The NO rate constant k on the Na$^+$-V$_2$O$_5$/TiO$_2$ catalyst decreased very sharply from 97.1 to 35.0 cm^3 g^{-1} s^{-1} with increasing Na/V molar ratio from 0.00 to 0.20. In comparison, k on the Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalyst remained almost unchanged when Ca/V molar ratio was below 0.05. Further increasing Ca/V molar ratio to 0.20 resulted in an obvious decrease of k from 101.8 to 46.3 cm^3 g^{-1} s^{-1}. It was suggested that Na$^+$ ions combined strongly with dispersed vanadia species, neutralized the Brønsted acid sites and reduced their reducibility. In comparison, Ca^{2+} ions slightly affected the Brønsted acid sites of catalyst. Besides, the dispersed vanadia species on the Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalyst had higher reducibility than Na$^+$-V$_2$O$_5$/TiO$_2$ catalyst. The different poisoning effects of Na$^+$ and Ca^{2+} ions doped on the V$_2$O$_5$/TiO$_2$ catalyst were correlated not only to the surface acidity but also to the reducibility of catalyst.

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1. Introduction

It is well known that the selective catalytic reduction (SCR) of nitric oxides with ammonia as reductant is one of the most successful method to eliminate NO$_x$ in flue gases from stationary sources, and the supported V$_2$O$_5$/TiO$_2$ catalysts promoted by WO$_3$ or MoO$_3$ have been practically used because of their high catalytic activity, high thermal stability and retardation of the SO$_2$ oxidation [1–4]. However, the V$_2$O$_5$/TiO$_2$ oxide based catalysts can be deactivated by deposition of alkali and alkaline earth metal salts in fly ashes. The effect of alkaline metals on the performance of V$_2$O$_5$/TiO$_2$ oxide based catalysts has been reported by many researchers [5–10] because of its practical interest. Shikada and Fujimoto [5] reported a remarkable increase of the catalytic activity of supported V$_2$O$_5$/TiO$_2$ catalysts by the addition of sodium or lithium salts and an activity decay of catalysts by the addition of potassium salt. In contrast, Kasaoka et al. [6] reported a suppressive effect on the catalytic activity of V$_2$O$_5$/TiO$_2$ catalysts by the addition of sodium salt. Bosch et al. [7] suggested that an alkaline metal such as lithium stabilizes the presence of tetravalent vanadium, resulting in an increase of SCR activity. Chen and

Yang [8] found a correlation between the SCR activity and the Brønsted acidity for a catalyst poisoned by alkaline metal oxides. Lietti et al. [9] suggested that potassium ions decrease the amount of ammonia adsorbed on V$_2$O$_5$/TiO$_2$, resulting in the decrease of both the number of acid sites on the catalyst and the activity of NO reduction. Kamata et al. [10] found that the strength and number of Brønsted acid sites decreased largely with the loading of K$_2$O in parallel with the decrease of the SCR activity, suggested that the SCR reaction involved NH$_3$ adsorption on Brønsted acid sites and potassium disturbed the formation of the active ammonia intermediates, NH$_4^+$, resulting in deactivation of the catalyst. Although great attention has been paid to the effect of alkaline metal ions on the surface acidity and SCR activity of catalysts, few studies have been devoted to the other properties than surface acidity. In fact, it has been established that the oxidative dehydrogenation of the adsorbed ammonia species by vanadia species is a key step in the SCR reaction [1,2,11–16], which is correlated to the reducibility of dispersed vanadia species on TiO$_2$. In this paper, the influence of sodium and calcium ions addition on the reducibility of vanadia species supported on anatase, as well as surface acidity of V$_2$O$_5$/TiO$_2$ catalyst, has been explored by using infrared spectroscopy of chemisorbed NH$_3$ (NH$_3$-IR), temperature-programmed desorption of NH$_3$ (NH$_3$-TPD), hydrogen temperature-programmed reduction (H$_2$-TPR) and UV–vis diffuse reflectance spectra (DRS) combined with micro-reactor test of selective

catalytic reduction of NO by NH$_3$, and the relationship between the surface properties and the catalytic activity of Na$^+$ or Ca^{2+} doped catalyst is discussed.

2. Experimental

2.1. Catalyst preparation

The anatase TiO$_2$ support was obtained by adding 0.125 mol TiCl$_4$ dropwise into 500 ml distilled water in an ice-water bath under stirring, followed by adding appropriate amount of 2 mol l^{-1} NH$_3$·H$_2$O until the pH value was higher than 9.0. Subsequently, the precipitate separated by filtering was repeatedly washed with distilled water to be free of chloride. The as-prepared gel was dried in air at 120 °C for about 12 h and calcined in air at 500 °C for 4 h.

The V$_2$O$_5$/TiO$_2$ catalyst with V$_2$O$_5$ loading of 3.87 wt% was prepared by impregnating the TiO$_2$ support with a aqueous solution containing the required amount of NH$_4$VO$_3$ dissolved in nitric acid (14 M) and the mixture was heated at 80 °C under stirring to mostly remove the water and then dried at 100 °C for about 12 h, calcined at 500 °C in air for 3 h. The catalyst thus prepared has a BET surface area of about 65.0 m^2 g^{-1} and a V$_2$O$_5$ loading of 0.655 mmol V/100 m^2 TiO$_2$.

The Na$^+$- and Ca^{2+}-doped V$_2$O$_5$/TiO$_2$ catalysts (denoted as Na$^+$-V$_2$O$_5$/TiO$_2$ and Ca^{2+}-V$_2$O$_5$/TiO$_2$ hereafter, respectively) with different molar ratios of Na/V and Ca/V were prepared by impregnating the V$_2$O$_5$/TiO$_2$ catalysts with the aqueous solutions containing the required amount of NaNO$_3$ or Ca (NO$_3$)$_2$, then dried in air at 100 °C for 12 h and calcined at 500 °C for 3 h.

2.2. Catalyst characterization

Temperature-programmed desorption of ammonia (NH$_3$-TPD) was carried out in a quartz U-tube reactor, detected with a thermal conductivity detector (TCD). About 0.25 g of powder catalyst was oxidized in flowing air (20 ml min^{-1}) at 500 °C for 0.5 h and cooled down to 150 °C. The samples were first saturated with pure NH$_3$ at 150 °C for 0.5 h, and after purging with flowing pure He (20 ml min^{-1}) until the TCD signal was stabilized, the samples were heated to 600 °C in flowing He (5 °C min^{-1}).

Infrared spectroscopy measurements of NH$_3$ adsorbed on the catalysts (NH$_3$-IR) were performed with a Nicolet 5700 FTIR spectrometer. The samples were pressed to self-supporting pieces with the same feeding-mass of samples. The samples were dried in flowing N$_2$ at 300 °C for 0.5 h, and then saturated with NH$_3$ at 100 °C for 0.5 h. After purging with N$_2$ at 100 °C for 1 h, the NH$_3$-IR spectra were recorded at 100 °C.

Hydrogen temperature-programmed reduction (H$_2$-TPR) was carried out in a quartz U-tube reactor. About 0.10 g sample was used. The H$_2$–Ar mixer (5 vol.% H$_2$) was switched on at a flowing rate of 20 ml min^{-1} and the temperature was increased linearly at a rate of 10 °C min^{-1}. The consumption of H$_2$ was detected by TCD and CuO powder was used as reference for quantitative analysis.

The UV–vis diffuse reflectance spectra (UV–vis DRS) of the Na$^+$- and Ca^{2+}-doped V$_2$O$_5$/TiO$_2$ catalysts were recorded on a Shimadzu UV-2401PC spectrophotometer using BaSO$_4$ as a reference at room temperature.

2.3. SCR activity measurements

The catalytic tests for the SCR of NO by NH$_3$ were carried out in a glass micro-reactor with catalyst samples of about 0.05 g and of 250–420 μm in diameter. Prior to the reaction, the sample was pretreated in flowing air at 500 °C for 0.5 h. The catalytic reaction was carried out at 310 °C and 0.1 Mpa, with a total flow rate 8.33 ml s^{-1} (ambient conditions) and GHSV = 9.6 × 10^5 h^{-1} (based on the total bed volume of catalyst samples). The inlet concentrations of reactants were 910 ppmv NO$_x$, 1000 ppmv NH$_3$, 4 vol.% O$_2$, and N$_2$ was the remainder. The NO concentrations before and after reaction were determined by using an N-(1-naphtyl)-ethylene-diamine dihydrochloride spectrophotometer method (Saltzman method) [17]. While working in excess of oxygen and with NH$_3$/NO (molar ratio) ≥1, the NO conversion rate for the SCR process can be supposed to first order reaction model in NO [1,18–20]. The deactivation of the catalyst was best described by the reaction rate constant k which was calculated according to the rate expression below [21,22]:

$$k = -\frac{F}{W}\ln(1 - X)$$

where k was the reaction rate constant based on mass of samples (cm^3 g^{-1} s^{-1}), F was the volume flow rate (ml s^{-1}), W was the catalyst mass (g), X was the fractional NO conversion.

3. Results and discussion

3.1. SCR activity

The SCR activities of Na$^+$-V$_2$O$_5$/TiO$_2$ and Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalysts with different Na$^+$ and Ca^{2+} loadings measured at 310 °C under steady state conditions are shown in Table 1, and the rate constant k as a function of Na$^+$ and Ca^{2+} loadings are shown in Fig. 1. It can be seen that k on the Na$^+$-V$_2$O$_5$/TiO$_2$ catalyst decreases very sharply from 97.1 to 35.0 cm^3 g^{-1} s^{-1} with increasing Na/V molar ratio from 0.00 to 0.20. In comparison, k on the Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalyst remains almost unchanged when Ca/V molar ratio is below 0.05. Further increasing Ca/V molar ratio to 0.20 results in an obvious decrease of k from 101.8 to 46.3 cm^3 g^{-1} s^{-1}, but the Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalyst has a higher SCR activity than the Na$^+$-V$_2$O$_5$/TiO$_2$ catalyst with the same loading of alkaline metal ions. These results indicate that addition of Na$^+$ and Ca^{2+} can poison the V$_2$O$_5$/TiO$_2$ catalyst for selective catalytic

Table 1
SCR activity at 310 °C for the poisoned V$_2$O$_5$/TiO$_2$ catalysts studied.

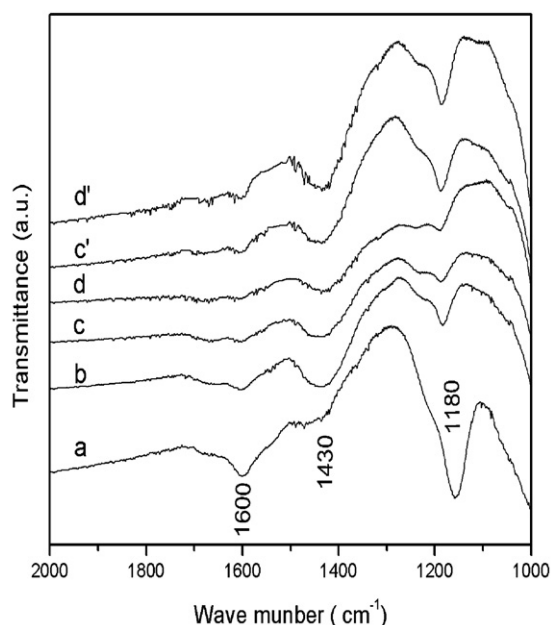| Catalyst	Na/V or Ca/V (mol mol^{-1})	Fractional NO conversion (mol mol^{-1})	Rate constant, k (cm^3 g^{-1} s^{-1})
V$_2$O$_5$/TiO$_2$	0.00	0.441	97.1
Na$^+$-V$_2$O$_5$/TiO$_2$	0.02	0.398	84.6
	0.05	0.340	69.3
	0.10	0.324	65.2
	0.20	0.189	35.0
Ca^{2+}-V$_2$O$_5$/TiO$_2$	0.02	0.434	94.8
	0.05	0.457	101.8
	0.10	0.409	87.6
	0.20	0.242	46.3
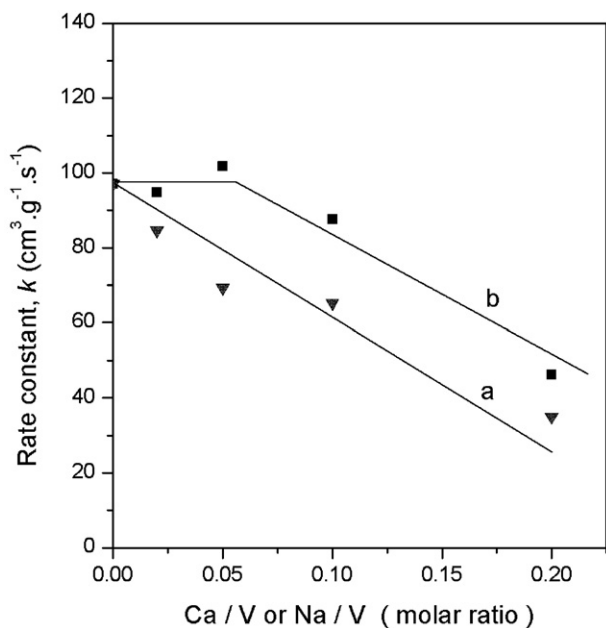
Fig. 1. SCR rate constant k at 310 °C for the V_2O_5/TiO_2 catalyst with different loading of Na^+ and Ca^{2+} loadings (a) Na^+-V_2O_5/TiO_2; (b) Ca^{2+}-V_2O_5/TiO_2.

Fig. 2. NH_3-IR spectra of Na^+-V_2O_5/TiO_2 and Ca^{2+}-V_2O_5/TiO_2 catalysts with different loadings of alkaline metal ions (a) TiO_2; (b) V_2O_5/TiO_2; Na^+-V_2O_5/TiO_2 with Na/V molar ratio of (c) 0.05; (d) 0.20; Ca^{2+}-V_2O_5/TiO_2 with Ca/V molar ratio of (c') 0.05; (d') 0.20.

reduction of NO by NH_3, and the Na^+ ions exhibit greater poisoning effect than Ca^{2+} ions. Chen and Yang [8] found that alkali metal ions were among the strongest poisons to the V_2O_5/TiO_2 catalyst for selective catalytic reduction of NO by NH_3, and the strength of the poison was directly related to its basicity. It is well known that Na_2O has a similar basicity to that of CaO. However, in our cases, these two poisons show different strength of the poison effect, suggesting that there is different chemical interaction of Na^+ and Ca^{2+} ions with the surface of V_2O_5/TiO_2 catalyst.

3.2. Surface acidity

It has been established that the surface acidity of V_2O_5/TiO_2 catalyst plays important roles in the selective catalytic reduction of NO by NH_3 [1,2,11–16], and the alkaline components can poison the acid sites of V_2O_5/TiO_2 catalysts, leading to deactivation of the catalysts [5–10,21–33]. In order to investigate the different poisoning effects of Na^+-V_2O_5/TiO_2 and Ca^{2+}-V_2O_5/TiO_2 catalysts, NH_3-IR spectroscopy was employed to elucidate the influence of Na^+ and Ca^{2+} on the acid sites of V_2O_5/TiO_2 catalyst, and the results are presented in Fig. 2. It can be seen that there are three absorption bands in the profiles of anatase TiO_2 support and V_2O_5/TiO_2 catalysts. Among them, The band at 1430 cm^{-1} is assigned to N–H bending vibration of NH_3 chemisorbed on Brønsted acid sites, while the bands at 1180 and 1600 cm^{-1} are assigned to N–H vibration of NH_3 chemisorbed on Lewis acid sites [10,11,15,16]. According to the kinetic mechanism proposed by Topsøe et al. [11,12], the SCR mechanism consists of two catalytic cycles. The important first step is chemisorption of NH_3 on the Brønsted acid site V–OH. With increase of Na^+ loading, the band intensities of Brønsted acid sites as well as Lewis acid sites decrease apparently (Fig. 2b–d). With increase of Ca^{2+} loading, the band intensity of Brønsted acid sites changed slightly (Fig. 2b, c' and d'), suggesting that Na^+ ions doped into the V_2O_5/TiO_2 catalyst neutralize Brønsted acid sites of the catalyst, while the Ca^{2+} ions doped into the V_2O_5/TiO_2 catalyst slightly affect the Brønsted acid sites of the catalyst. It seems reasonable to argue that the different poisoning effect of Na^+ and Ca^{2+} ions on the V_2O_5/TiO_2 catalyst for selective catalytic reduction of NO by NH_3 is correlated to the different surface acidity of catalyst.

Fig. 3 presents the NH_3-TPD profiles of Na^+-V_2O_5/TiO_2 and Ca^{2+}-V_2O_5/TiO_2 catalysts with different loading of alkaline metal ions. Only a broad peak around 270 °C can be observed in the profile of anatase TiO_2 support (Fig. 3a). For the supported V_2O_5/TiO_2 catalyst, the intensity of desorption peak around 270 °C increases and a new desorption peak appears around 450 °C (Fig. 3b), indicating that the dispersed vanadia species on surface of anatase TiO_2 constitutes two kinds of acid sites, *i.e.*, weak acid sites and strong acid sites. Our previous studies have confirmed that dispersion capacity of vanadium oxide on anatase (a complete
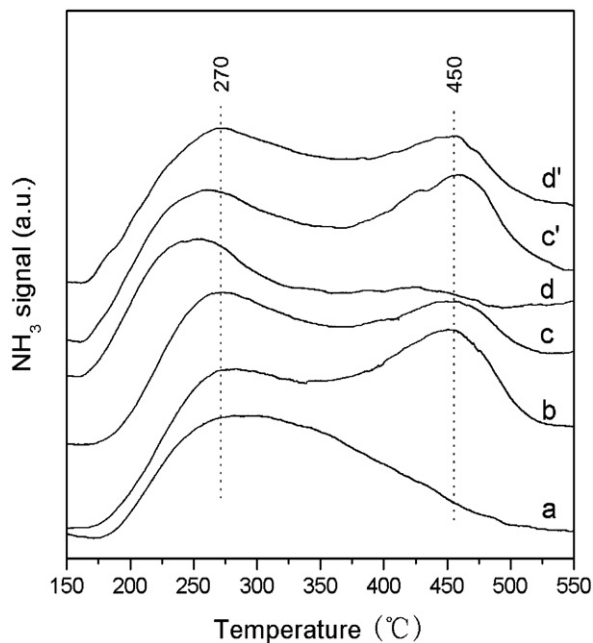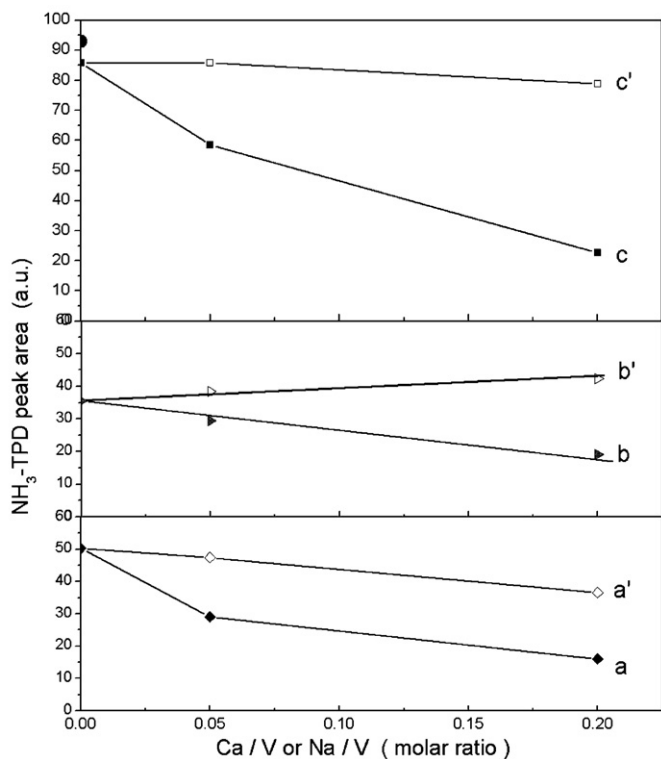

Fig. 3. NH_3-TPD profiles of Na^+-V_2O_5/TiO_2 and Ca^{2+}-V_2O_5/TiO_2 catalysts (a) TiO_2; (b) V_2O_5/TiO_2; Na^+-V_2O_5/TiO_2 with Na/V molar ratio of (c) 0.05; (d) 0.20; Ca^{2+}-V_2O_5/TiO_2 with Ca/V molar ratio of (c') 0.05; (d') 0.20.

monolayer) is 1.14 mmol V/100 m^2 TiO$_2$ [34]. For the V$_2$O$_5$/TiO$_2$ catalyst with vanadium ion loading of 0.655 mmol V/100 m^2 TiO$_2$ studied in this work, the bare fraction of anatase TiO$_2$ support and its contribution to NH$_3$-TPD peak area can be estimated. By subtracting this contribution, the NH$_3$-TPD peak area of dispersed vanadia species can be calculated, which represents the amount of acid sites constituted by vanadia species, and the results are shown in Fig. 4. It can be seen that with increase of Na$^+$ loading the amount of weak acid sites and strong acid sites decreases simultaneously, indicating that the weak acid sites and strong acid sites are neutralized by the doped Na$^+$ ions. In contrast, with increase of Ca^{2+} loading, the amount of weak acid sites increases at the expense of strong acid sites, indicating that the Ca^{2+} ions doped only react with the strong acid sites on the catalyst and reduce their acid strength. The total amount of acid sites remains almost unchanged when Ca/V molar ratio is below 0.05. Further increase of Ca^{2+} loading results in a slight decrease of total amount of acid sites. According to the results obtained by Lisi et al. [30], the strong acid sites adsorbing ammonia at $T > 350\,°C$ are not involved in the SCR reaction occurring at lower temperatures. The results of our study indicate that the weak acid sites on the V$_2$O$_5$/TiO$_2$ catalyst are neutralized by the doped Na$^+$ ions, leading to decrease of amount of weak acid sites on the catalyst and thus remarkable decrease of SCR activity. It is noteworthy that the IR band intensity of Brønsted acid sites changed slightly (Fig. 2b, c' and d'), and the amount of weak acid sites slightly increases with increase of Ca^{2+} loading (Fig. 4b'), but the NO rate constant on the Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalyst decrease more rapidly when Ca/V molar ratio is higher than 0.05. Apparently, the poisoning effect of alkaline metal ions doped on the V$_2$O$_5$/TiO$_2$ catalyst cannot be explained only by surface acidity of catalyst. The influence of doping alkaline metal ions on the interaction between dispersed vanadia species and TiO$_2$ support should be taken into consideration.

3.3. Reducibility of dispersed vanadia species

It has been also established that the oxidative dehydrogenation of the adsorbed ammonia species by vanadia species is another key step in the SCR of NO by NH$_3$ [1,2,11–16]. To investigate the effects of doping Na$^+$ and Ca^{2+} ions on the interaction of dispersed vanadia species with TiO$_2$ support and on the reduction behaviors of dispersed vanadia species, the H$_2$-TPR profiles of V$_2$O$_5$/TiO$_2$ catalysts with different loadings of Na$^+$ and Ca^{2+} ions are shown in Fig. 5. As shown by profile (Fig. 5a), a H$_2$ consumption peak has been observed for pure TiO$_2$ around 640 °C, corresponding to the reduction of Ti^{4+} → Ti^{3+} in the surface layers of TiO$_2$. Profile (Fig. 5a') of pure V$_2$O$_5$ has two reduction peaks located at 700 and 730 °C, corresponding to the following stepwise reduction of the vanadium oxide [35], respectively: V$_2$O$_5$ → 1/3 V$_6$O$_{13}$ → 2VO$_2$. In comparison with pure V$_2$O$_5$, the main feature of the TPR profiles of the V$_2$O$_5$/TiO$_2$ samples is the obvious shift of their reduction peaks to lower temperature region, as shown in profile (Fig. 5b), revealing the fact that, comparatively, the supported vanadia species are easier to be reduced due to strong interaction between dispersed vanadia species and TiO$_2$ support. As shown in the profiles of Fig. 5c–f and c'–f', when Na$^+$ and Ca^{2+} were doped into the V$_2$O$_5$/TiO$_2$ catalysts, the H$_2$ consumption peak shifts to apparently higher temperatures with the increase of loading, implying the corresponding drop in the reducibility of the vanadium ions in these samples. However, it is hard to evaluate the different effects of Na$^+$ and Ca^{2+} ions on the reducibility of the vanadium ions in supported vanadium oxide directly from their TPR profiles as no obvious difference in peak positions can be visualized from the profiles. In this respect, more information can be obtained from the H$_2$ consumption of each vanadium ion as shown in Fig. 6, which decreases rapidly when Na/V and Ca/V molar ratios are higher than 0.05, indicating that doping Na$^+$ and Ca^{2+} ions into the V$_2$O$_5$/TiO$_2$ catalyst reduce the reduction degree of vanadium ions. Interestingly, the Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalyst has a higher reduction degree


Fig. 4. NH$_3$-TPD peak area of Na$^+$-V$_2$O$_5$/TiO$_2$ and Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalysts (●) TiO$_2$; Na$^+$-V$_2$O$_5$/TiO$_2$: (a) strong acid sites; (b) weak acid sites; (c) total acid sites; Ca^{2+}-V$_2$O$_5$/TiO$_2$: (a') strong acid sites; (b') weak acid sites; (c') total acid sites.
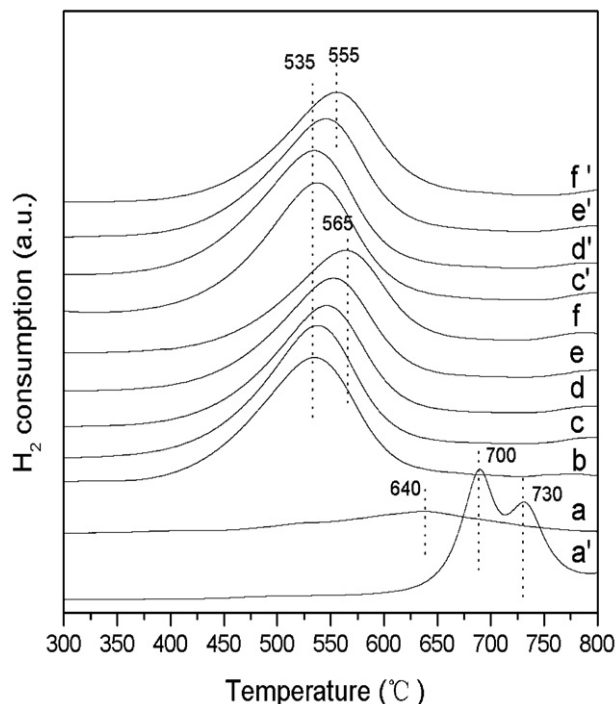
Fig. 5. TPR profiles of V$_2$O$_5$/TiO$_2$ catalysts with different loadings of alkaline metal ions (a) TiO$_2$; (a') V$_2$O$_5$; (b) V$_2$O$_5$/TiO$_2$; Na$^+$-V$_2$O$_5$/TiO$_2$ with Na/V molar ratio of (c) 0.02; (d) 0.05; (e) 0.10; (f) 0.20; Ca^{2+}-V$_2$O$_5$/TiO$_2$ with Ca/V molar ratio of (c') 0.02; (d') 0.05; (e') 0.10; (f') 0.20.
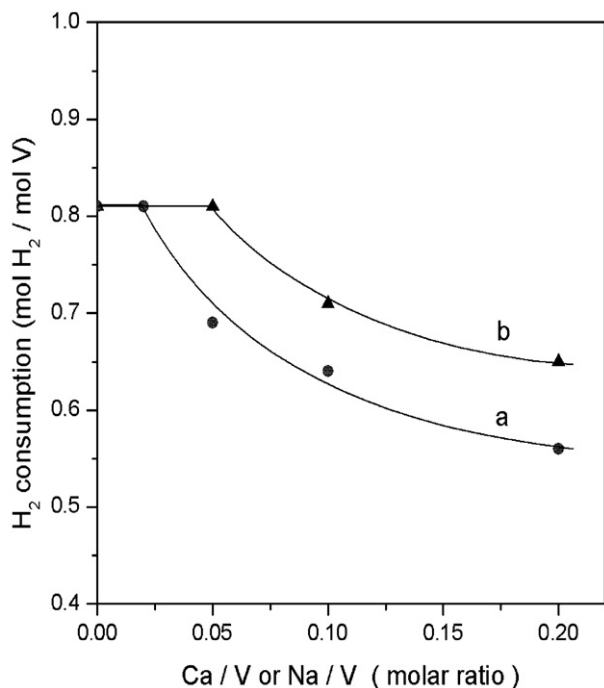
Fig. 6. Average H$_2$ consumption of each vanadium ion in the V$_2$O$_5$/TiO$_2$ catalysts with different loadings of alkaline metal ions (a) Na$^+$-V$_2$O$_5$/TiO$_2$; (b) Ca^{2+}-V$_2$O$_5$/TiO$_2$.

Fig. 7. UV–vis DR spectra of Na$^+$-V$_2$O$_5$/TiO$_2$ and Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalysts (a) TiO$_2$; (a′) V$_2$O$_5$; (b) V$_2$O$_5$/TiO$_2$; Na$^+$-V$_2$O$_5$/TiO$_2$ with Na/V molar ratio of (c) 0.05; (d) 0.20; Ca^{2+}-V$_2$O$_5$/TiO$_2$ with Ca/V molar ratio of (c′) 0.05; (d′) 0.20.
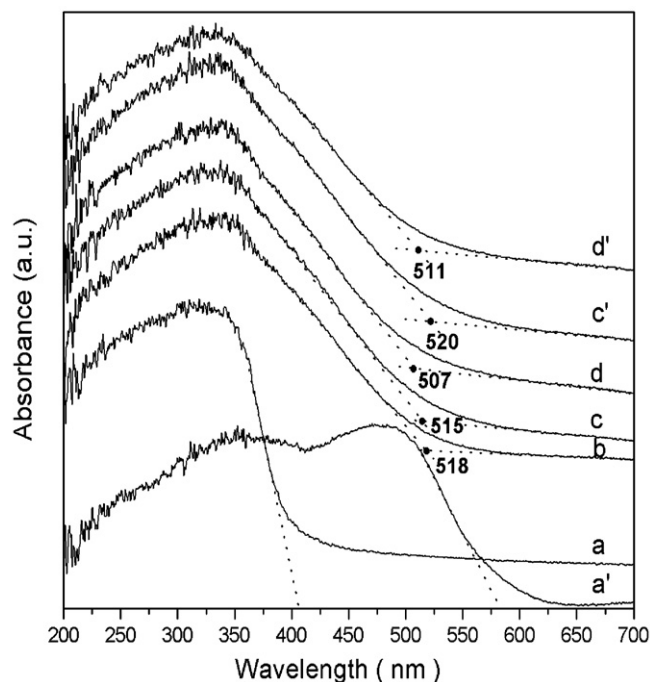
than the Na$^+$-V$_2$O$_5$/TiO$_2$ catalyst with the same loading of alkali metal ions, which is also correlated to the SCR activity.

3.4. Surface interaction

In order to elucidate the interaction between the alkaline components and V$_2$O$_5$/TiO$_2$ catalyst, the UV–vis DR spectra of the Na$^+$-V$_2$O$_5$/TiO$_2$ and Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalysts are presented in Fig. 7. TiO$_2$ support (Fig. 7a) absorbs in the ultraviolet region, 320–350 nm, due to an electron transition from valence band to a higher band [36,37], while the absorption band of bulk V$_2$O$_5$ oxides largely expands to the visible region (Fig. 7a′), which is associated to charge transfer transitions from the O$_{2p}$ valence band to the empty V$_{3d}$ [36,38]. For the V$_2$O$_5$/TiO$_2$ sample (Fig. 7b), the characteristic band of bulk V$_2$O$_5$ oxide centered at 550 nm disappeared, indicating that vanadia species are highly dispersed in the V$_2$O$_5$/TiO$_2$ catalyst studied. It has been found that UV–vis adsorption edge position of V$_2$O$_5$/TiO$_2$ catalyst is sensitive to the coordination structure of vanadia species, and that the higher the absorption edge wavelength, the higher the coordination of polymeric vanadia species [36–39]. In our cases, it can be seen that when doping Na$^+$ ions into the V$_2$O$_5$/TiO$_2$ catalyst (Fig. 7c and d), the UV–vis absorption edge position of V$_2$O$_5$/TiO$_2$ catalyst decrease from 518 nm to 515 and 507 nm, suggesting that the Na$^+$ ions combine strongly with dispersed vanadia species and reduce their poly-merization degree, leading to the lower reducibility and thus lower SCR activity. In comparison, when doping Ca^{2+} ions into the V$_2$O$_5$/TiO$_2$ catalyst (Fig. 7c′ and d′), the UV–vis adsorption edge position decrease slightly (from 518 nm to 520 and 511 nm), implying that the Ca^{2+} ions combine weakly with dispersed vanadia species and the Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalyst has higher reducibility and thus higher SCR activity than the Na$^+$-V$_2$O$_5$/TiO$_2$ catalyst.

4. Conclusions

Based on the above experimental results and discussion, one can conclude that deposition of Na$^+$ and Ca^{2+} ions can poison the V$_2$O$_5$/TiO$_2$ catalyst for selective catalytic reduction of NO by NH$_3$, and the Na$^+$ ions exhibit greater poisoning effect than Ca^{2+} ions. Na$^+$ ions combine strongly with dispersed vanadia species and neutralize the Brønsted acid sites and reduce their reducibility, leading to the remarkable decrease of SCR activity. In comparison, Ca^{2+} ions combine weakly with dispersed vanadia species and slightly affect the Brønsted acid sites of the catalyst. Besides, the dispersed vanadia species on the Ca^{2+}-V$_2$O$_5$/TiO$_2$ catalyst has higher reducibility than Na$^+$-V$_2$O$_5$/TiO$_2$ catalyst. The different poisoning effects of Na$^+$ and Ca^{2+} ions doped on the V$_2$O$_5$/TiO$_2$ catalyst for selective catalytic reduction of NO by NH$_3$ are correlated not only to the surface acidity of catalyst but also to the reducibility of dispersed vanadia species.

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